

INFLUENCE OF OXYGEN ON THE PHASE SEPARATION OF CHALCOGENIC GLASSES

ЕМИЛИЯ ШЛЕКОВА*, ЮРАГ ДОУРОВОС*, БРАТИСЛАВА

Amorphous selenium and the chalcogenic glass of the type $Ge_xTe_nAs_m$, the structure of which remains homogeneous at whatever temperature, disintegrate in the state of undercooled liquid under the influence of the oxygen atmosphere, or after the direct incorporation of oxygen into the matrix, giving the original matrix and the phase characterized by oxygen. The new phase of the undercooled liquid crystallizes regularly at a lower temperature, the amount of it being related to that of the oxygen incorporated.

ВЛИЯНИЕ КИСЛОРОДА НА РАЗДЕЛЕНИЕ ФАЗ ХАЛЬКОГЕННЫХ СТЕКОЛ

Аморфный селен и халькогенное стекло типа $Ge_xTe_nAs_m$, структура которых остается однородной при любой температуре, переходят в состояние переохлажденной жидкости под влиянием атмосферного кислорода или при введении кислорода в кристаллическую решетку, давая оригинальную решетку и фазу, характеризующуюся кислородом. Эта новая фаза переохлажденной жидкости кристаллизуется регулярно при более низкой температуре, которая оказывается связанной с величиной введенного кислорода.

I. INTRODUCTION

Recently there have been a few articles reporting that some admixtures or impurities, e.g. oxygen [1, 2], arsenium [3], tellurium [4], sulphur [5] etc. change the elementary physical properties of chalcogenic glasses. The consistent analysis of the influence of these elements has not yet been made.

In this article the thermophysical characteristics of amorphous selenium, of the chalcogenic glasses, related to the eutectical $Ge_{15}Te_{85}$ and other materials, were studied by the DTA method. The samples produced on air, in the argon atmosphere and in a reducing medium gave different results concerning the shape of the thermograms. By direct incorporation of oxygen into the structure in question, the authors have found that the changes characterized by splitting the exotherm of crystallization are caused by the chemisorption of oxygen.

* Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta, 899 30 BRATISLAVA, Czechoslovakia.

II. MATERIAL AND METHOD

The samples of the chalcogenic glasses were made from 99.999 % pure starting elements (As_2O_3 was of 99.9 %) by direct fusing in a silica ampoule evacuated to 10^{-5} torr.

The reduction of the remaining oxygen in one series of samples was carried out for 24 hours at 1000 °C by means of a graphite layer, which coated the inner walls of the silica ampoule. The coating was made by wetting the inner walls by benzene without toluene and by heating up to 1100 °C. After homogenizing at 1000 °C, the fused material was cooled to room temperature with a speed of 100 °C/sec.

The amorphous selenium was melted at 620 °C, homogenized for 2 hours and cooled at a speed of 400 °C/sec. up to the temperature of liquid nitrogen.

The powders of the samples prepared in this way were subjected to a thermal analysis with the help of the commercial Thermal Analyser 900 made by DU PONT. The weights of the samples were (10 ± 0.1) mg, the rate of the temperature increase 10 °C/min. The crucible effects were reduced by using polished handles of a 100 μ thickness for the sample part, as well as for the reference. The measurements were made in the atmosphere of argon and in air, respectively. The device was calibrated between (295—675) °C by first class standards delivered by the National Bureau of Standards ICTA.

III. RESULTS AND DISCUSSION

The time dependent influence of different atmospheres on the characteristics of the amorphous samples was investigated by the DTA method.

III. 1. Selenium

The thermogram of amorphous selenium taken immediately after its production is characterized by the softening region near the temperature $T_w \sim 40$ °C (the transformation point is defined as the inflex point of the related "S" dependence), by the exotherm of crystallization with a maximum about $T_x \sim 155$ °C and melting about $T_m \sim 215$ °C. The amorphous selenium has been powdered and exposed to the influence of air at 20 °C. The related thermograms of the transformation regions shown in Fig. 1 correspond with the different times of ageing "t".

The evolution of the relaxation processes, the so called ageing, or maturing of the structure of the amorphous selenium [6] is characterized by the saturated character of the stabilization of the transformation temperature from 40 °C to 51 °C. The endotherm has a deeping tendency.

The relaxation processes in the vicinity of the transformation temperature are

not caused by the atmosphere. The samples of selenium made in the same way by heat in air, in an argon atmosphere or stored in the vacuum for the same length of time are characterized always by the thermograms from Fig. 1.

On the contrary, the exotherm of crystallization of Se (Fig. 2) shows distinct differences of the samples after annealing in air at 30 °C, when compared with the samples made in the vacuum or in the atmosphere of inert gases. In the former case

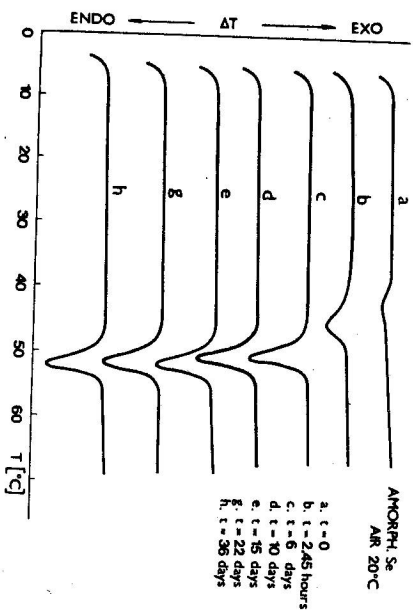


Fig. 1. Thermograms of the transformation regions of amorphous Se: a) $t = 0$, b) $t = 2$ hours 45 min., c) $t = 6$ days, d) $t = 10$ days, e) $t = 15$ days, f) $t = 22$ days, g) $t = 36$ days, h) $t = 36$ days.

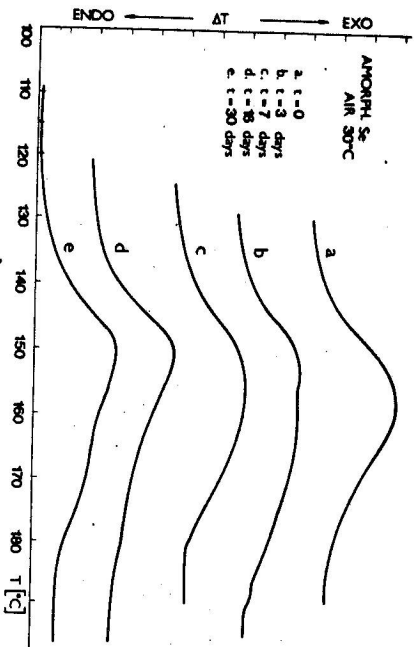


Fig. 2. Thermograms of crystallization regions of amorphous Se: a) $t = 0$, b) $t = 3$ days, c) $t = 7$ days, d) $t = 16$ days, e) $t = 30$ days.

a separation of the crystallization exotherm into two exotherms is suggested, with maxima at temperatures of $T_1 \sim 153$ °C and $T_2 \sim 165$ °C, caused by ageing. The atmospheric oxygen is incorporated step by step into the amorphous matrix, influencing its structure and its state in such a way that it becomes able to separate. According to the results shown in Fig. 1, the phase separation of Se takes place only in the undercooled liquid. Each of the liquid phases crystallizes separately in this case.

Fig. 2 shows how one original phase, the pure manufactured selenium, separates into two phases during ageing. Afterwards, the quantity of the phase enriched by oxygen from the air increases step by step at the cost of the original "high temperature phase".

We have found that this process is caused by the atmosphere. The thermograms of the samples elaborated in the same way in the vacuum and in the inert gases, respectively, are always characterized by the dependence a) in Fig. 2, i.e. the disintegration of the undercooled liquid into two phases does not take place in such a selenium. Therefore we explained the separation of the crystallization effects by the influence of atmospheric oxygen.

III. 2. The Ge-Te-As system

More detailed observations of the influence of oxygen were made on a glassforming chalcogenic system Ge-Te-As. In this system, we incorporated step by step during manufacturing oxygen bound in As_2O_3 in such a way as to preserve the arsenic content unchanged.

The thermogram DTA of the system $Ge_{1-x}Te_{81}As_{(4-x)}(As_2O_3)_x$ for $x = 0$, i.e. that of the not oxygenized chalcogenic glass, which has been, moreover, produced in the mentioned way in a reducing medium can be found in Fig. 3a. It is characterized by a softening region about the temperature of $T_w \sim 130$ °C and by a simple course of the crystallization exotherm with a maximum at a temperature of $T_m \sim 730$ °C.

Glass of the same composition, but manufactured in the common way described in literature (e.g. [7, 8], i.e. in a silica ampoule in a vacuum of 10^{-5} torr, without the reducing medium), is characterized under the same experimental conditions by a thermogram showing the beginning of the phase separation (Fig. 3). This gets more striking if it is measured in the medium of air (Fig. 3c). The process of the phase separation depends evidently on the concentration of oxygen in the sample (Fig. 4). The enthalpy of the exothermic reaction at a lower temperature, is related to the amount of the oxygen incorporated into the amorphous material.

IV. CONCLUSION

The authors observed that amorphous selenium, chalcogenic morecomponent materials, but also other glasses prepared in a common way in the air or exposed to

its influence, are characterized by different results on the thermograms if compared with the same glasses manufactured in the vacuum or in an inert atmosphere. The materials belonging to the first group disintegrate into two individually crystallizing phases, into the phase of the original glass and into the phase enriched by another sorbed material. Comparing the phenomenon with the influence of oxygen directly

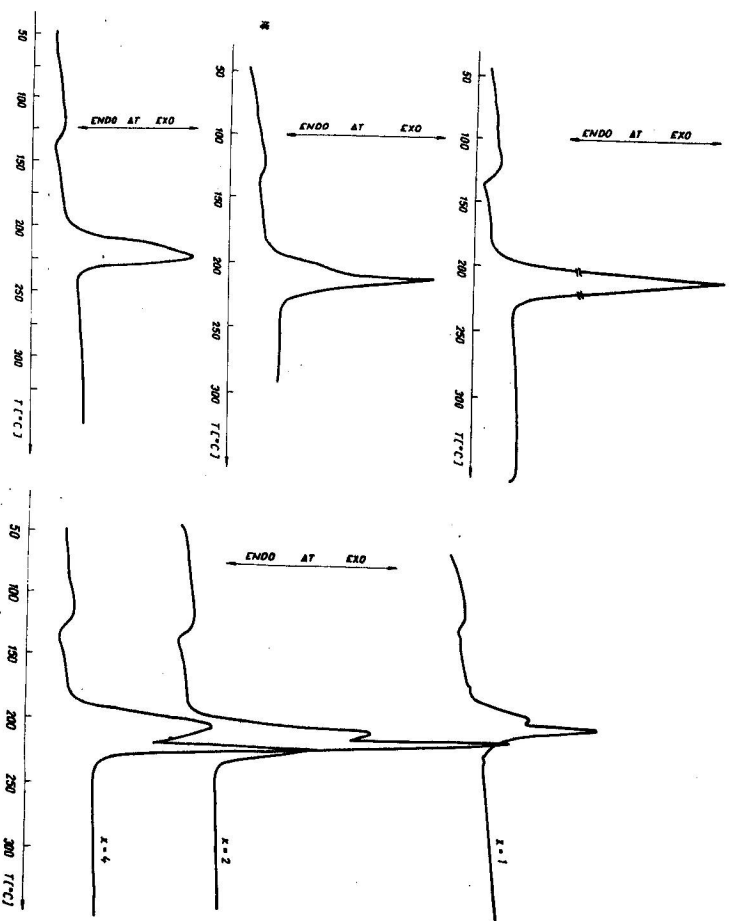


Fig. 3. Thermograms of the amorphous $Ge_{15}Te_{81}As_4$, prepared and measured in different media: a) prepared in a reducing medium, measured in an argon atmosphere; b) prepared without a reducing medium, measured in an argon atmosphere; c) prepared without a reducing medium, measured in air.

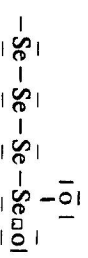
Fig. 4. Thermograms of amorphous $Ge_{15}Te_{81}As_{(4-x)}(As_2O_3)_{x/2}$ for a) $x = 1$; b) $x = 2$; c) $x = 4$.

incorporated into the structure, the authors showed that this reaction was caused by chemisorption of oxygen from the air.

Amorphous materials contain a large number of the so-called "dangling bonds" and of unsaturated bonds, as a consequence of rapid cooling [9]. In the case of

chalcogenic glasses, it is especially oxygen characterized by a considerably higher activity than the other components, which is able of chemisorption (e.g. from the atmosphere) to satisfy partly these claims. This causes changes of the electric conductivity, of the absorption edge, of the crystallization temperature etc. [10, 11, 12]. On the contrary, in the samples maturing in an inert medium the bonds remain disturbed or they pair with one another, as it was observed by Webb and Brodie [12].

The history of the material and the concentration of the chemisorbed oxygen in the amorphous Se [11] determines if the arising SeO_2 remains in the soluble unstable monomeric form, or if it forms a polymeric structure dissolved in the original matrix. Oxygen can break the bonds of the selenium chains and can bind itself at their ends by stronger chemical bonds (energy of the bonds $E_{O-Se} = 82$ kcal/mol; $E_{Se-Se} = 66$ kcal/mol [13]). According to the model in [14], two oxygens are always bound at the end of the selenium chain, giving rise to one hole. It could be expected that the more active oxygen will saturate its bond



by taking one electron from the neighbouring selenium. The step by step migrating hole forms the weakest place in the chain. Probably the continuous structure SeO_2 is formed with the increasing oxygen concentration, which is torn away from the selenium chains.

The phase separation process influences the stability of the material in the amorphous matter, together with many of its physical and chemical features. In studying the chalcogenic glasses, it is necessary to expect, besides the natural separation caused by the chemical composition, also a so-called secondary phase separation as a consequence of the manufacturing, storing or processing of the material in air or in another oxygen containing medium.

REFERENCES

- [1] Lacourse W. C., Twaddell V. A., McKenzie J. D., *J. Non Cryst. Solids* 3 (1970), 234.
- [2] Bagley B. G., Di Salvo F. J., Bair H. E., Vogel E. M., *Phys. Stat. Sol.* 11 (1965), 891.
- [3] Bagley B. G., Di Salvo F. J., Bair H. E., Vogel E. M., *Proc. 5th Int. Conf. Am. and Liq. Sem. Garnich-Partenkirchen* 1973.
- [4] Audiere J. P., *J. Thermal Anal.* 6 (1974), 27.
- [5] Iakov A. S., *Ser. fir. tek. i mat. nauk Izv. AN Azerb. SSR*, 1 (1964), 83.
- [6] Doupovec J., Králová B., Illeková E., (to be published).
- [7] Iizima S., Sugi M., Kikuchi M., *Solid St. Comm.* 8 (1970), 153.
- [8] Fritzsche H., Ovshinski S. R., *J. Non Cryst. Solids* 2 (1970), 148.
- [9] Moss, *Graczk. Phys. Rev.* 23 (1969), 1164.

- [10] Twaddell W. A., LaCourse W. C., Mackenzie J. D., *J. Non Cryst. Solids* 8—10 (1972), 831.
- [11] Vaško A., Ležal D., Srb I., *J. Non Cryst. Sol.* 4 (1970), 311.
- [12] Webb J. B., Brodie D. E., *Can. J. Phys.* 51 (1973), 493.
- [13] Vedenejev V. L., Gurvič L. V., Kondrajev V. N., Medvedev V. A., Frankievic E. L., *Energie razryva chimitskich svyazef*, Moskva 1962.
- [14] Mackenzie J. D., *J. Non Cryst. Sol.* 2 (1970), 16.

Received May 14th, 1975